

CLAIMS

WHAT IS CLAIMED IS:

1. A polymerization process comprising contacting one or more monomer(s), one or more Lewis acid(s), one or more initiator(s), and a diluent comprising one or more hydrofluorocarbon(s) (HFC's) in a reactor.
2. The process of claim 1, wherein one or more hydrofluorocarbon(s) is represented by the formula: $C_xH_yF_z$ wherein x is an integer from 1 to 40 and y and z are integers of one or more.
3. The process of claim 2, wherein x is from 1 to 10.
4. The process of claim 2, wherein x is from 1 to 6.
5. The process of claim 2, wherein x is from 1 to 3.
6. The process of claim 1, wherein the one or more hydrofluorocarbon(s) is independently selected from the group consisting of fluoromethane; difluoromethane; trifluoromethane; fluoroethane; 1,1-difluoroethane; 1,2-difluoroethane; 1,1,1-trifluoroethane; 1,1,2-trifluoroethane; 1,1,1,2-tetrafluoroethane; 1,1,2,2-tetrafluoroethane; 1,1,1,2,2-pentafluoroethane; 1-fluoropropane; 2-fluoropropane; 1,1-difluoropropane; 1,2-difluoropropane; 1,3-difluoropropane; 2,2-difluoropropane; 1,1,1-trifluoropropane; 1,1,2-trifluoropropane; 1,1,3-trifluoropropane; 1,2,2-trifluoropropane; 1,2,3-trifluoropropane; 1,1,1,2-tetrafluoropropane; 1,1,1,3-tetrafluoropropane; 1,1,2,2-tetrafluoropropane; 1,1,2,3-tetrafluoropropane; 1,1,3,3-tetrafluoropropane; 1,2,2,3-tetrafluoropropane; 1,1,1,2,2-pentafluoropropane; 1,1,1,2,3-pentafluoropropane; 1,1,1,3,3-pentafluoropropane; 1,1,2,2,3-pentafluoropropane; 1,1,2,3,3-pentafluoropropane; 1,1,1,2,2,3-hexafluoropropane; 1,1,1,2,3,3-

hexafluoropropane;	1,1,1,3,3,3-hexafluoropropane;	1,1,1,2,2,3,3-
heptafluoropropane;	1,1,1,2,3,3,3-heptafluoropropane;	1-fluorobutane;
2-fluorobutane;	1,1-difluorobutane;	2-difluorobutane;
1,3-difluorobutane;	1,4-difluorobutane;	2,2-difluorobutane;
2,3-difluorobutane;	1,1,1-trifluorobutane;	1,1,1-trifluorobutane;
1,1,2-trifluorobutane;	1,1,3-trifluorobutane;	1,1,4-trifluorobutane;
1,2,2-trifluorobutane;	1,2,3-trifluorobutane;	1,3,3-trifluorobutane;
1,2,3-trifluorobutane;	1,1,1,2-tetrafluorobutane;	1,1,1,3-tetrafluorobutane;
1,1,1,4-tetrafluorobutane;	1,1,2,2-tetrafluorobutane;	1,1,2,3-tetrafluorobutane;
1,1,2,4-tetrafluorobutane;	1,1,3,3-tetrafluorobutane;	1,1,3,4-tetrafluorobutane;
1,1,4,4-tetrafluorobutane;	1,2,2,3-tetrafluorobutane;	1,2,2,3-tetrafluorobutane;
1,2,3,4-tetrafluorobutane;	2,2,3,3-tetrafluorobutane;	1,1,1,2,2-pentafluorobutane;
1,1,1,2,3-pentafluorobutane;	1,1,1,2,4-pentafluorobutane;	1,1,1,3,3-pentafluorobutane;
1,1,1,3,4-pentafluorobutane;	1,1,1,4,4-pentafluorobutane;	1,1,2,2,3-pentafluorobutane;
1,1,2,2,4-pentafluorobutane;	1,1,2,4,4-pentafluorobutane;	1,1,2,3,3-pentafluorobutane;
1,1,2,4,4-pentafluorobutane;	1,2,2,3,3-pentafluorobutane;	1,1,3,3,4-pentafluorobutane;
1,2,2,3,4-pentafluorobutane;	1,1,1,2,2,3-hexafluorobutane;	1,1,1,2,2,4-hexafluorobutane;
1,1,1,2,3,3-hexafluorobutane,	1,1,1,2,3,4-hexafluorobutane;	1,1,1,2,3,4-hexafluorobutane;
1,1,1,2,4,4-hexafluorobutane;	1,1,1,3,4,4-hexafluorobutane;	1,1,1,3,3,4-hexafluorobutane;
1,1,1,3,4,4-hexafluorobutane;	1,1,2,2,3,3-hexafluorobutane;	1,1,1,4,4,4-hexafluorobutane;
1,1,2,2,3,3-hexafluorobutane;	1,1,2,2,4,4-hexafluorobutane;	1,1,2,2,3,4-hexafluorobutane;
1,1,2,2,4,4-hexafluorobutane;	1,1,1,2,3,4,4-hexafluorobutane;	1,1,2,3,3,4-hexafluorobutane;
1,1,1,2,3,4,4-hexafluorobutane;	1,1,1,2,2,3,3-heptafluorobutane;	1,1,1,2,2,4,4-heptafluorobutane;
1,1,1,2,2,3,4-heptafluorobutane;	1,1,1,2,2,3,4-heptafluorobutane;	1,1,1,2,3,3,4-heptafluorobutane;
1,1,1,2,3,4,4-heptafluorobutane;	1,1,1,3,3,4,4-heptafluorobutane;	1,1,1,2,4,4,4-heptafluorobutane;
1,1,1,3,3,4,4-heptafluorobutane;	1,1,1,2,2,3,3-octafluorobutane;	1,1,1,2,2,3,3,4-octafluorobutane;
1,1,1,2,2,3,3-octafluorobutane;	1,1,1,2,2,4,4-octafluorobutane;	1,1,1,2,3,3,4,4-octafluorobutane;
1,1,1,2,2,4,4-octafluorobutane;	1,1,1,2,2,3,3,4,4-nonafluorobutane;	1,1,1,2,2,3,4,4,4-nonafluorobutane;

nonafluorobutane; 1-fluoro-2-methylpropane; 1,1-difluoro-2-methylpropane; 1,3-difluoro-2-methylpropane; 1,1,1-trifluoro-2-methylpropane; 1,1,3-trifluoro-2-methylpropane; 1,3-difluoro-2-(fluoromethyl)propane; 1,1,1,3-tetrafluoro-2-methylpropane; 1,1,3,3-tetrafluoro-2-methylpropane; 1,1,3-trifluoro-2-(fluoromethyl)propane; 1,1,1,3,3-pentafluoro-2-methylpropane; 1,1,3,3-tetrafluoro-2-(fluoromethyl)propane; 1,1,1,3-tetrafluoro-2-(fluoromethyl)propane; fluorocyclobutane; 1,1-difluorocyclobutane; 1,2-difluorocyclobutane; 1,3-difluorocyclobutane; 1,1,2-trifluorocyclobutane; 1,1,3-trifluorocyclobutane; 1,2,3-trifluorocyclobutane; 1,1,2,2,3-tetrafluorocyclobutane; 1,1,3,3-tetrafluorocyclobutane; 1,1,2,2,3,3-pentafluorocyclobutane; 1,1,2,3,3-hexafluorocyclobutane; 1,1,2,2,3,4-hexafluorocyclobutane; 1,1,2,3,3,4-hexafluorocyclobutane; 1,1,2,2,3,3,4-heptafluorocyclobutane; vinyl fluoride; 1,1-difluoroethene; 1,2-difluoroethene; 1,1,2-trifluoroethene; 1-fluoropropene; 1,1-difluoropropene; 1,2-difluoropropene; 1,3-difluoropropene; 2,3-difluoropropene; 3,3-difluoropropene; 1,1,2-trifluoropropene; 1,1,3-trifluoropropene; 1,2,3-trifluoropropene; 1,3,3-trifluoropropene; 2,3,3-trifluoropropene; 3,3,3-trifluoropropene; 1-fluoro-1-butene; 2-fluoro-1-butene; 3-fluoro-1-butene; 4-fluoro-1-butene; 1,1-difluoro-1-butene; 1,2-difluoro-1-butene; 1,3-difluoropropene; 1,4-difluoro-1-butene; 2,3-difluoro-1-butene; 2,4-difluoro-1-butene; 3,3-difluoro-1-butene; 3,4-difluoro-1-butene; 4,4-difluoro-1-butene; 1,1,2-trifluoro-1-butene; 1,1,3-trifluoro-1-butene; 1,1,4-trifluoro-1-butene; 1,2,3-trifluoro-1-butene; 1,2,4-trifluoro-1-butene; 1,3,3-trifluoro-1-butene; 1,3,4-trifluoro-1-butene; 1,4,4-trifluoro-1-butene; 2,3,3-trifluoro-1-butene; 2,3,4-trifluoro-1-butene; 2,4,4-trifluoro-1-butene; 3,3,4-trifluoro-1-butene; 3,4,4-trifluoro-1-butene; 4,4,4-trifluoro-1-butene; 1,1,2,3-tetrafluoro-1-butene; 1,1,2,4-tetrafluoro-1-butene; 1,1,3,3-tetrafluoro-1-butene; 1,1,3,4-tetrafluoro-1-butene; 1,1,4,4-tetrafluoro-1-butene; 1,2,3,3-tetrafluoro-1-butene; 1,2,3,4-tetrafluoro-1-butene; 1,2,4,4-tetrafluoro-1-butene; 1,3,3,4-tetrafluoro-1-butene; 1,3,4,4-tetrafluoro-1-butene; 1,4,4,4-tetrafluoro-1-

butene; 2,3,3,4-tetrafluoro-1-butene; 2,3,4,4-tetrafluoro-1-butene; 2,4,4,4-tetrafluoro-1-butene; 3,3,4,4-tetrafluoro-1-butene; 3,4,4,4-tetrafluoro-1-butene; 1,1,2,3,3-pentafluoro-1-butene; 1,1,2,3,4-pentafluoro-1-butene; 1,1,2,4,4-pentafluoro-1-butene; 1,1,3,3,4-pentafluoro-1-butene; 1,1,3,4,4-pentafluoro-1-butene; 1,1,4,4,4-pentafluoro-1-butene; 1,2,3,3,4-pentafluoro-1-butene; 1,2,4,4,4-pentafluoro-1-butene; 2,3,3,4,4-pentafluoro-1-butene; 2,3,4,4,4-pentafluoro-1-butene; 3,3,4,4,4-pentafluoro-1-butene; 1,1,2,3,3,4-hexafluoro-1-butene; 1,1,2,4,4,4-hexafluoro-1-butene; 1,2,3,3,4,4-hexafluoro-1-butene; 1,2,3,4,4,4-hexafluoro-1-butene; 2,3,3,4,4,4-hexafluoro-1-butene; 1,1,2,3,4,4-heptafluoro-1-butene; 1,1,3,3,4,4-heptafluoro-1-butene; 1,2,3,3,4,4,4-heptafluoro-1-butene; 1-fluoro-2-butene; 2-fluoro-2-butene; 1,1-difluoro-2-butene; 1,2-difluoro-2-butene; 1,3-difluoro-2-butene; 1,4-difluoro-2-butene; 2,3-difluoro-2-butene; 1,1,1-trifluoro-2-butene; 1,1,2-trifluoro-2-butene; 1,1,3-trifluoro-2-butene; 1,1,4-trifluoro-2-butene; 1,2,3-trifluoro-2-butene; 1,2,4-trifluoro-2-butene; 1,1,1,2-tetrafluoro-2-butene; 1,1,1,3-tetrafluoro-2-butene; 1,1,1,4-tetrafluoro-2-butene; 1,1,2,3-tetrafluoro-2-butene; 1,1,2,4-tetrafluoro-2-butene; 1,2,3,4-tetrafluoro-2-butene; 1,1,1,2,3-pentafluoro-2-butene; 1,1,1,2,4-pentafluoro-2-butene; 1,1,1,3,4-pentafluoro-2-butene; 1,1,1,4,4-pentafluoro-2-butene; 1,1,2,3,4-pentafluoro-2-butene; 1,1,1,2,4,4-hexafluoro-2-butene; 1,1,1,3,4,4-hexafluoro-2-butene; 1,1,1,4,4,4-hexafluoro-2-butene; 1,1,2,3,4,4-hexafluoro-2-butene; 1,1,1,2,3,4,4-heptafluoro-2-butene; 1,1,1,2,4,4,4-heptafluoro-2-butene; and mixtures thereof.

7. The process of claim 1, wherein the one or more hydrofluorocarbon(s) is independently selected from the group consisting of fluoromethane, difluoromethane, trifluoromethane, 1,1-difluoroethane, 1,1,1-trifluoroethane, 1,1,1,2-tetrafluoroethane, and mixtures thereof.

8. The process of any of claims 1 to 7, wherein the diluent comprises from 15 to 100 volume % HFC based upon the total volume of the diluent.
9. The process of claim 8, wherein the diluent comprises from 20 to 100 volume % HFC based upon the total volume of the diluent.
10. The process of claim 9, wherein the diluent comprises from 25 to 100 volume % HFC based upon the total volume of the diluent.
11. The process of any of claims 1 to 10, wherein the diluent further comprises a hydrocarbon, a non-reactive olefin, and/or an inert gas.
12. The process of claim 11, wherein the hydrocarbon is a halogenated hydrocarbon other than an HFC.
13. The process of claim 12, wherein the halogenated hydrocarbon is methyl chloride.
14. The process of any of claims 1 to 13, wherein the one or more Lewis acid(s) is represented by the formula MX_4 ;
wherein M is a Group 4, 5, or 14 metal; and
each X is a halogen.
15. The process of any of claims 1 to 13, wherein the one or more Lewis acid(s) is represented by the formula MR_nX_{4-n} ;
wherein M is Group 4, 5, or 14 metal;
each R is a monovalent C_1 to C_{12} hydrocarbon radical independently selected from the group consisting of an alkyl, aryl, arylalkyl, alkylaryl and cycloalkyl radicals;
 n is an integer from 0 to 4; and
each X is a halogen.

16. The process of any of claims 1 to 13, wherein the one or more Lewis acid(s) is represented by the formula $M(RO)_nR'mX_{4-(m+n)}$; wherein M is Group 4, 5, or 14 metal; each RO is a monovalent C₁ to C₃₀ hydrocarboxy radical independently selected from the group consisting of an alkoxy, aryloxy, arylalkoxy, alkylaryloxy radicals; each R' is a monovalent C₁ to C₁₂ hydrocarbon radical independently selected from the group consisting of an alkyl, aryl, arylalkyl, alkylaryl and cycloalkyl radicals; n is an integer from 0 to 4; m is an integer from 0 to 4, wherein the sum of n and m is not more than 4; and each X is a halogen.
17. The process of any of claims 1 to 13, wherein the one or more Lewis acid(s) is represented by the formula $M(RC=OO)_nR'mX_{4-(m+n)}$; wherein M is Group 4, 5, or 14 metal; each RC=OO is a monovalent C₂ to C₃₀ hydrocarbacyl radical independently selected from the group consisting of an alkacyloxy, arylacyloxy, arylalkylacyloxy, alkylarylaceyloxy radicals; each R' is a monovalent C₁ to C₁₂ hydrocarbon radical independently selected from the group consisting of an alkyl, aryl, arylalkyl, alkylaryl and cycloalkyl radicals; n is an integer from 0 to 4; m is an integer from 0 to 4, wherein the sum of n and m is not more than 4; and each X is a halogen.
18. The process of any of claims 1 to 13, wherein the one or more Lewis acid(s) is represented by the formula MOX₃; wherein M is a Group 5 metal; and

each X is a halogen.

19. The process of any of claims 1 to 13, wherein the one or more Lewis acid(s) is represented by the formula MX_3 ;
wherein M is a Group 13 metal; and
each X is a halogen.
20. The process of any of claims 1 to 13, wherein the one or more Lewis acid(s) is represented by the formula MR_nX_{3-n} ;
wherein M is a Group 13 metal;
each R is a monovalent C₁ to C₁₂ hydrocarbon radical independently selected from the group consisting of an alkyl, aryl, arylalkyl, alkylaryl and cycloalkyl radicals;
 n is an integer from 1 to 3; and
each X is a halogen.
21. The process of any of claims 1 to 13, wherein the one or more Lewis acid(s) is represented by the formula $M(RO)_nR'_mX_{3-(m+n)}$;
wherein M is a Group 13 metal;
each RO is a monovalent C₁ to C₃₀ hydrocarboxy radical independently selected from the group consisting of an alkoxy, aryloxy, arylalkoxy, alkylaryloxy radicals;
each R' is a monovalent C₁ to C₁₂ hydrocarbon radical independently selected from the group consisting of an alkyl, aryl, arylalkyl, alkylaryl and cycloalkyl radicals;
 n is an integer from 0 to 3;
 m is an integer from 0 to 3, wherein the sum of n and m is from 1 to 3; and
each X is a halogen.
22. The process of any of claims 1 to 13, wherein the one or more Lewis acid(s) is represented by the formula $M(RC=OO)_nR'_mX_{3-(m+n)}$;
wherein M is a Group 13 metal;

each RC=OO is a monovalent hydrocarbacyl radical independently selected from the group independently selected from the C_2 to C_{30} group consisting of an alkacyloxy, arylacyloxy, arylalkylacyloxy, alkylarylcyclaxy radicals;

each R' is a monovalent C_1 to C_{12} hydrocarbon radical independently selected from the group consisting of an alkyl, aryl, arylalkyl, alkylaryl and cycloalkyl radicals;

n is an integer from 0 to 3;

m is an integer from 0 to 3, wherein the sum of n and m is from 1 to 3; and each X is a halogen.

23. The process of any of claims 1 to 13, wherein the one or more Lewis acid(s) is represented by the formula MX_y ;
wherein M is a Group 15 metal;
each X is a halogen; and
 y is 3, 4 or 5.
24. The process of any of claims 1 to 13, wherein the one or more Lewis acid(s) is represented by the formula $\text{MR}_n\text{X}_{y-n}$;
wherein M is a Group 15 metal;
each R is a monovalent C_1 to C_{12} hydrocarbon radical independently selected from the group consisting of an alkyl, aryl, arylalkyl, alkylaryl and cycloalkyl radicals;
 n is an integer from 0 to 4;
 y is 3, 4 or 5, wherein n is less than y; and
each X is a halogen.
25. The process of any of claims 1 to 13, wherein the one or more Lewis acid(s) is represented by the formula $\text{M}(\text{RO})_n\text{R}'_m\text{X}_{y-(m+n)}$;
wherein M is a Group 15 metal,

- each RO is a monovalent C₁ to C₃₀ hydrocarboxy radical independently selected from the group consisting of an alkoxy, aryloxy, arylalkoxy, alkylaryloxy radicals;
- each R' is a monovalent C₁ to C₁₂ hydrocarbon radical independently selected from the group consisting of an alkyl, aryl, arylalkyl, alkylaryl and cycloalkyl radicals;
- n is an integer from 0 to 4;
- m is an integer from 0 to 4;
- y is 3, 4 or 5, wherein the sum of n and m is less than y; and each X is a halogen.
26. The process of any of claims 1 to 13, wherein the one or more Lewis acid(s) is represented by the formula M(RC=OO)_nR'_mX_{y-(m+n)};
wherein M is a Group 15 metal;
each RC=OO is a monovalent C₂ to C₃₀ hydrocarbacyloxy radical independently selected from the group consisting of an alkacyloxy, arylacyloxy, arylalkylacyloxy, alkylarylacyloxy radicals;
each R' is a monovalent C₁ to C₁₂ hydrocarbon radical independently selected from the group consisting of an alkyl, aryl, arylalkyl, alkylaryl and cycloalkyl radicals;
n is an integer from 0 to 4;
m is an integer from 0 to 4;
y is 3, 4 or 5, wherein the sum of n and m is less than y; and each X is a halogen.
27. The process of any of claims 1 to 13, wherein the one or more Lewis acid(s) is independently selected from the group consisting of titanium tetrachloride, titanium tetrabromide, vanadium tetrachloride, tin tetrachloride, zirconium tetrachloride, titanium bromide trichloride, titanium dibromide dichloride, vanadium bromide trichloride, tin chloride trifluoride, benzyltitanium trichloride, dibenzyltitanium dichloride, benzylzirconium trichloride, dibenzylzirconium dibromide, methyltitanium

trichloride, dimethyltitanium difluoride, dimethyltin dichloride, phenylvanadium trichloride, methoxytitanium trichloride, n-butoxytitanium trichloride, di(isopropoxy)titanium dichloride, phenoxytitanium tribromide, phenylmethoxyzirconium trifluoride, methyl methoxytitanium dichloride, methyl methoxytin dichloride, benzyl isopropoxyvanadium dichloride, acetoxytitanium trichloride, benzoylzirconium tribromide, benzyloxytitanium trifluoride, isopropoxyloxytin trichloride, methyl acetoxytitanium dichloride, benzyl benzyloxyvanadium chloride, vanadium oxytrichloride, aluminum trichloride, boron trifluoride, gallium trichloride, indium trifluoride, ethylaluminum dichloride, methylaluminum dichloride, benzylaluminum dichloride, isobutylgallium dichloride, diethylaluminum chloride, dimethylaluminum chloride, ethylaluminum sesquichloride, methylaluminum sesquichloride, trimethylaluminum, triethylaluminum, methoxyaluminum dichloride, ethoxyaluminum dichloride, 2,6-di-tert-butylphenoxyaluminum dichloride, methoxy methylaluminum chloride, 2,6-di-tert-butylphenoxy methylaluminum chloride, isopropoxygallium dichloride, phenoxy methylindium fluoride, acetoxyaluminum dichloride, benzoyloxyaluminum dibromide, benzoyloxygallium difluoride, methyl acetoxyaluminum chloride, isopropoxyindium trichloride, antimony hexachloride, antimony hexafluoride, arsenic pentafluoride, antimony chloride pentafluoride, arsenic trifluoride, bismuth trichloride arsenic fluoride tetrachloride, tetraphenylantimony chloride, triphenylantimony dichloride, tetrachloromethoxyantimony, dimethoxytrichloroantimony, dichloromethoxyarsine, chlorodimethoxyarsine, difluoromethoxyarsine, acetatotetrachloroantimony, (benzoato) tetrachloroantimony, and bismuth acetate chloride.

28. The process of any of claims 1 to 13, wherein the one or more Lewis acid(s) is independently selected from the group consisting of aluminum trichloride, aluminum tribromide, ethylaluminum dichloride, ethylaluminum sesquichloride, diethylaluminum chloride,

methylaluminum dichloride, methylaluminum sesquichloride, dimethylaluminum chloride, boron trifluoride, and titanium tetrachloride.

29. The process of any of claims 1 to 28, wherein the one or more initiator(s) comprise a hydrogen halide, a carboxylic acid, a carboxylic acid halide, a sulfonic acid, an alcohol, a phenol, a polymeric halide, a tertiary alkyl halide, a tertiary aralkyl halide, a tertiary alkyl ester, a tertiary aralkyl ester, a tertiary alkyl ether, a tertiary aralkyl ether, an alkyl halide, an aryl halide, an alkylaryl halide or an arylalkylacid halide.
30. The process of any of claims 1 to 28, wherein the one or more initiator(s) is independently selected from the group consisting of HCl, H₂O, methanol, (CH₃)₃CCl, C₆H₅C(CH₃)₂Cl, (2-Chloro-2,4,4-trimethylpentane) and 2-chloro-2-methylpropane.
31. The process of any of claims 1 to 28, wherein the one or more initiator(s) is independently selected from the group consisting of hydrogen chloride, hydrogen bromide, hydrogen iodide, acetic acid, propanoic acid, butanoic acid; cinnamic acid, benzoic acid, 1-chloroacetic acid, dichloroacetic acid, trichloroacetic acid, trifluoroacetic acid, p-chlorobenzoic acid, p-fluorobenzoic acid, acetyl chloride, acetyl bromide, cinnamyl chloride, benzoyl chloride, benzoyl bromide, trichloroacetylchloride, trifluoroacetylchloride, p-fluorobenzoylchloride, methanesulfonic acid, trifluoromethanesulfonic acid, trichloromethanesulfonic acid, p-toluenesulfonic acid, methanesulfonyl chloride, methanesulfonyl bromide, trichloromethanesulfonyl chloride, trifluoromethanesulfonyl chloride, p-toluenesulfonyl chloride, methanol, ethanol, propanol, 2-propanol, 2-methylpropan-2-ol, cyclohexanol, benzyl alcohol, phenol, 2-methylphenol, 2,6-dimethylphenol, p-chlorophenol, p-fluorophenol, 2,3,4,5,6-pentafluorophenol, and 2-hydroxynaphthalene.

32. The process of any of claims 1 to 28, wherein the one or more initiator(s) is independently selected from the group consisting of 2-chloro-2,4,4-trimethylpentane; 2-bromo-2,4,4-trimethylpentane; 2-chloro-2-methylpropane; 2-bromo-2-methylpropane; 2-chloro-2,4,4,6,6-pentamethylheptane; 2-bromo-2,4,4,6,6-pentamethylheptane; 1-chloro-1-methylethylbenzene; 1-chloroadamantane; 1-chloroethylbenzene; 1, 4-bis(1-chloro-1-methylethyl) benzene; 5-tert-butyl-1,3-bis(1-chloro-1-methylethyl) benzene; 2-acetoxy-2,4,4-trimethylpentane; 2-benzoyloxy-2,4,4-trimethylpentane; 2-acetoxy-2-methylpropane; 2-benzoyloxy-2-methylpropane; 2-acetoxy-2,4,4,6,6-pentamethylheptane; 2-benzoyl-2,4,4,6,6-pentamethylheptane; 1-acetoxy-1-methylethylbenzene; 1-aceotxyadamantane; 1-benzoyloxyethylbenzene; 1,4-bis(1-acetoxy-1-methylethyl) benzene; 5-tert-butyl-1,3-bis(1-acetoxy-1-methylethyl) benzene; 2-methoxy-2,4,4-trimethylpentane; 2-isopropoxy-2,4,4-trimethylpentane; 2-methoxy-2-methylpropane; 2-benzyloxy-2-methylpropane; 2-methoxy-2,4,4,6,6-pentamethylheptane; 2-isopropoxy-2,4,4,6,6-pentamethylheptane; 1-methoxy-1-methylethylbenzene; 1-methoxyadamantane; 1-methoxyethylbenzene; 1,4-bis(1-methoxy-1-methylethyl) benzene; 5-tert-butyl-1,3-bis(1-methoxy-1-methylethyl) benzene, and 1,3,5-tris(1-chloro-1-methylethyl) benzene.
33. The process of any of claims 1 to 32, wherein the one or more initiator(s) further comprise a weakly-coordinating anion.
34. The process of any of claims 1 to 33, wherein the process is substantially absent of water.
35. The process of any of claims 1 to 33, wherein the one or more initiator(s) comprise greater than 30 ppm water (based upon weight).
36. The process of any of claims 1 to 35, wherein the one or more monomer(s) is independently selected from the group consisting of olefins, alpha-

olefins, disubstituted olefins, isoolefins, conjugated dienes, non-conjugated dienes, styrenics, substituted styrenics, and vinyl ethers.

37. The process of claim 36, wherein the one or more monomer(s) is independently selected from the group consisting of styrene, para-alkylstyrene, para-methylstyrene, alpha-methyl styrene, divinylbenzene, diisopropenylbenzene, isobutylene, 2-methyl-1-butene, 3-methyl-1-butene, 2-methyl-2-pentene, isoprene, butadiene, 2,3-dimethyl-1,3-butadiene, β -pinene, myrcene, 6,6-dimethyl-fulvene, hexadiene, cyclopentadiene, methyl cyclopentadiene, piperylene, methyl vinyl ether, ethyl vinyl ether, and isobutyl vinyl ether.
38. The process of any of claims 1 to 37, wherein the reactor is independently selected from the group consisting of a continuous flow stirred tank reactor, a plug flow reactor, a moving belt or drum reactor, a jet or nozzle reactor, a tubular reactor, a batch reactor, and an autorefrigerated boiling-pool reactor.
39. The polymerization process of any of claims 1 to 38, wherein the diluent has a dielectric constant greater than 10 at -85°C.
40. The process of claim 39, wherein the dielectric constant is greater than 20 at -85°C.
41. The process of claim 40, wherein the dielectric constant is greater than 25 at -85°C.
42. The process of claim 41, wherein the dielectric constant is greater than 40 at -85°C.
43. The polymerization process of any of claims 1 to 42 to form a polymer having a diluent mass uptake of less than 4 wt%.

44. The process of claim 43, wherein the polymer has a diluent mass uptake of less than 3 wt%.
45. The process of claim 44, wherein the polymer has a diluent mass uptake of less than 2 wt%.
46. The process of claim 45, wherein the polymer has a diluent mass uptake of less than 1 wt%.
47. The process of claim 46, wherein the polymer has a diluent mass uptake of less than 0.5 wt%.
48. The polymerization process of any of claims 1, 8-10 or 14-47, the diluent comprising methyl chloride and one or more hydrofluorocarbon(s) independently selected from the group consisting of difluoromethane, 1,1-difluoroethane, and 1,1,1,2-tetrafluoroethane.
49. The process of claim 48 wherein the diluent further comprises a non-reactive olefin, one or more other hydrocarbons, and/or an inert gas.
50. The polymerization process of any of claims 1 to 49, the process comprising the steps of:
reacting the one or more monomer(s) in the presence of one or more Lewis acid(s), one or more initiator(s), and a diluent comprising one or more hydrofluorocarbon(s) (HFC's); and
withdrawing the polymer from the reactor.
51. The polymerization process of any of claims 1 to 49, the process comprising the steps of:
 - (a) introducing one or more monomer(s) into a reactor;
 - (b) adding one or more Lewis acid(s) and one or more initiator(s);

- (c) introducing a diluent comprising one or more hydrofluorocarbon(s) (HFC's); and
 - (d) withdrawing a polymer from the reactor.
52. The polymerization process of claim 1 or any of claims 2 to 49 in which particles of polymer are polymerized using a catalyst system and a diluent comprising one or more hydrofluorocarbon(s) (HFC's).
53. The polymerization process of claim 1 or any of claims 2 to 49 in which particles of polymer are polymerized in a slurry using a carbocationic catalyst system and a diluent comprising one or more hydrofluorocarbon(s) (HFC's).
54. The polymerization process of claim 1 or any of claims 2 to 39 or 43 to 49 in which particles of polymer are polymerized using a catalyst system and a diluent, the diluent having a dielectric constant greater than 18.50 at -85°C.
55. The process of claim 54, wherein the dielectric constant is greater than 19.00 at -85°C.
56. The process of claim 55, wherein the dielectric constant is greater than 20.00 at -85°C.
57. The process of claim 56, wherein the dielectric constant is greater than 25.00 at -85°C.
58. The process of claim 57, wherein the dielectric constant is greater than 30.00 at -85°C.

59. The process of claim 58, wherein the dielectric constant is greater than 35.00 at -85°C.
60. The process of claim 59, wherein the dielectric constant is greater than 40.00 at -85°C.
61. The process of any of claims 54 to 60, wherein the diluent is independently selected from the group consisting of at least one of a hydrofluorocarbon or a blend of a hydrofluorocarbon and methyl chloride.
62. A polymerization process in which particles of polymer are polymerized using a diluent comprising one or more hydrofluorocarbon(s) (HFC's).
63. A composition comprising the product obtainable by the polymerization process of any of claims 1, 2 to 49, 50, 51, or any of claims 52 to 62.
64. A polymerization medium suitable to polymerize one or more monomer(s) to form a polymer, the polymerization medium comprising one or more Lewis acid(s), one or more initiator(s), and a diluent comprising one or more hydrofluorocarbon(s) (HFC's).
65. The polymerization medium of claim 64, wherein the one or more monomer(s), the one or more Lewis acid(s), the one or more initiator(s), the diluent, and the one or more hydrofluorocarbon(s) are defined as in any of claims 1 to 49 or 54 to 61.
66. A homopolymer, copolymer, or terpolymer obtainable by the process of any of claims 1 to 49, 50, 51, 52 to 62, or by the use of the polymerization medium of claims 64 or 65, or by the composition of claim 63.
67. The homopolymer, copolymer, or terpolymer of claim 66, wherein the polymer has a Mw greater than 10,000.

68. The homopolymer, copolymer, or terpolymer of claim 67, wherein the polymer has a Mw greater than 50,000.
69. The homopolymer, copolymer, or terpolymer of claim 68, wherein the polymer has a Mw greater than 100,000.